half the acid solution had been added. At measured intervals 5-ml. aliquots of the reaction mixture were removed for analysis with a pipet calibrated by weight with the acid solution at the desired temperature. Each sample was run directly into 50 ml. of isopropyl alcohol containing 2 ml. of saturated aqueous sodium iodide under carbon dioxide. The analysis was continued as described above. Data for a typical pair of measurements at 40° in a mixture containing 0.05 mole of *p*-toluenesulfonic acid per kilogram of solution are given in Table II. Because of the greater ease of the graphical method, it was generally employed for the calculation of the rate constants. Occasional checks with the least squares method showed excellent agreement.

Stoichiometry of the Reaction.—Because of interference in the phenol determination due to acetylation in the acetic acid solution, aqueous ethanol was employed as solvent for quantitative determination of the phenol and acetone formed in the reaction. A solution of 7.3707 g. (0.0464 mole) of 95.6% w. cumene hydroperoxide in fifty weight per cent. aqueous ethanol containing 0.5 mole of *p*-toluenesulfonic acid per kilogram of solution was maintained at 60 ± 1° for 80 minutes. An equal volume of distilled water was added, the pressure was reduced to 125 mm., and the mixture was distilled through a ten-inch, helices-packed column. Analysis showed the distillate to contain 0.0260 mole of acetone[7] (2,4-dinitrophenylhydrazone m.p. 125–126°; lit. m.p. 126°) and 0.0052 mole of phenol[8] (2,4,6-tribromo derivative, m.p. 95.5–6.0°; lit. m.p. 96°); and the residue to contain 0.0246 mole of phenol and 0.0141 mole of unreacted peroxide. The yield of phenol was 92.3% and of acetone, 80.5%.

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[7] This procedure, a modification of the hydroxylamine hydrochloride method of M. Marasco (*Ind. Eng. Chem.*, **18**, 701 (1926)), is described in "Methyl Ethyl Ketone, Its Uses and Data on Its Properties," Shell Chemical Corp., San Francisco, California, 1938, p. 45.

[8] L. Lykken, R. S. Treseder and V. Zahn, *Ind. Eng. Chem., Anal. Ed.*, **18**, 103 (1946).

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

Gas Production in the Photolysis of Liquid Methyl Iodide[1]

BY ROBERT H. SCHULER[2] AND CHESTER T. CHMIEL

RECEIVED FEBRUARY 20, 1953

The importance of "Hot Radical" processes in the photolysis of liquid methyl iodide is further evidenced in the formation of methane and ethane as gaseous products. For the reactions induced by light at 2537 Å. the quantum yield for the formation of methane is 0.023, while that of ethane is 0.007. Although the iodine concentration is increasing during the course of the reaction, the ethane and methane yields are found to be independent of the extent of irradiation. The gas yields are dependent upon iodine concentration only at very high iodine concentrations. At room temperature, these yields are independent of the temperature of the sample. Methylene iodide is shown to be a product of the photolysis, while little or no hydrogen, ethylene, or acetylene formation is observed.

Previously Hamill and Schuler[3] and Schultz and Taylor[4] have concluded from studies, respectively, of the liquid and vapor phase photolysis of methyl iodide that it is necessary to assume as part of the mechanism certain reactions which are independent of the iodine concentration and of the temperature of the system. This led to a proposed mechanism which bases the net observed products on reactions occurring as a result of the excess kinetic energy given to the methyl radicals in the photolytic step. These hot radical processes must take place before this excess energy has been entirely redistributed by collision with the surrounding molecules.

This investigation was undertaken in order to determine the effect of iodine on the production of methane and ethane in the liquid phase photolysis. Since iodine does not interfere with the required analyses, investigation of the gas production reactions allows a study of the iodine dependence of the processes over a much wider range of iodine concentrations than was possible in the iodine production measurements. This work also serves as the basis for a comparative study of gas production in the X-ray decomposition of methyl iodide.[5]

Experimental

Methyl Iodide.—Both commercially obtained C.P. methyl iodide and a laboratory preparation (from methanol, phosphorus and iodine) were used in this investigation. The samples were washed with thiosulfate and water, dried with silica gel, and carefully fractionated through a three-foot helix-packed column. The center cut boiling at 42.4° was taken and, when kept in the dark, found to be without decomposition over periods of many months. All samples were found to have a refractive index ($n^{25}D$) of 1.5271–1.5272. A total of 9 different fractions from 5 preparations was used with no apparent discrepancies being traceable to the individual samples.

Ultraviolet Source.—A 50-watt Hanovia SC-2537 helical low pressure mercury discharge lamp was used. This was operated from the laboratory a.c. line through a variac and high voltage transformer. The intensity was monitored in terms of a constant lamp current of 50 ma. The input to the transformer at this setting was 3.3 amperes at 97–98 volts. A small centrifugal blower was used to circulate air over the sample tube and lamp in order to keep these at room temperature and remove any ozone formed. There was very little increase in the temperature of the system with this arrangement.

Cells.—The cell used for a major part of the work consisted of a 12-mm. quartz tube with a graded seal to Pyrex and an attached high vacuum stopcock. Five ml. of methyl iodide was placed in this tube, the sample degassed, the vapor region masked to restrict the activation to the liquid phase, and the sample irradiated for the desired period in the center of the lamp helix.

A second cell, which permitted thermostating of the sample during the irradiation, consisted of a jacketed tube to which a quartz window was cemented with silver chloride and the seal made vacuum tight with Glyptal. A side tube and stopcock, through which the tube could be evacuated, were arranged at angles of 120° to the cell axis. By rotating the assembly, the side arm could be employed in the freezing of the sample during the degassing and measuring operations. The sample was irradiated with the cell in a vertical position and with the window facing the end of the

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[1] This work was supported, in part, under Contract AT(30-1)-1084 with the U. S. Atomic Energy Commission. Presented at the 121st Meeting of the American Chemical Society in Buffalo, N. Y., March 25, 1952.

[2] Brookhaven National Laboratory, Upton, N. Y.

[3] W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

[4] R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950).

[5] R. C. Petry and R. H. Schuler, THIS JOURNAL, **75**, 3796 (1953).

lamp helix. The transmission of the window of this cell was determined before the assembly of the cell to be 84% at 2537 Å.

The irradiation given a particular sample was determined from the period of irradiation at constant intensity, with the intensity defined in terms of the iodine produced in the photodecomposition of ethyl iodide. For actinometric purposes, the quantum yield of this latter reaction is taken as $\phi_I = 0.40$ (iodine atoms per quantum absorbed) on the basis of Norton's results.[6] As the absorption coefficients of the alkyl iodides are very high at 2537 Å., all of the light transmitted through the window is absorbed in a relatively thin region adjacent to the window.

Gas Measurement—Methane.—The sample to be irradiated was degassed on a high vacuum line by freezing in liquid nitrogen (−196°) and pumping off the residual gas. The sample was then warmed to room temperature, bubbled, frozen and pumped again. This was repeated four times or until the residual gas amounted to 10^{-8} mole or less. Liquid nitrogen on a trap between the sample tube and Toepler pump prevented the condensation of mercury. After irradiation, the sample tube was attached to the line and the sample frozen in liquid nitrogen. The methane was then pumped to a McLeod gage for measurement. It was found that a single degassing of the sample in this manner recovered upwards of 90% of the methane formed in the photolysis with an additional 5–10% being obtained in subsequent degassings. The gas after measurement could then be allowed to expand into a modified Saunders–Taylor apparatus and a suitable portion taken for combustion analysis.[7]

Gas Measurement—Ethane.—Ethane was obtained by degassing the sample at ethyl bromide mush temperature (∼ −115°). Higher temperatures must be avoided here because of the appreciable vapor pressure of methyl iodide. The fractionation was carried out in two steps, the first with the trap at liquid nitrogen temperature and the cell at −115°, and then, after the ethane had been accumulated in the trap (with the fraction volatile at liquid nitrogen temperature being pumped off and added to the methane measurement), the trap was raised to −115° and the ethane pumped to the McLeod gage and measured. The ethane was found to degas very slowly from the sample under these conditions. Because of this a total of at least 8–10 degassings were required to remove the major fraction of ethane which, together with the relatively low ethane yield, made the resultant accuracy of measurement rather poor.

Gas Analysis.—Representative samples of the material volatile at −196° were transferred to the Saunders–Taylor apparatus. Hydrogen was determined by burning the sample over copper oxide at 275°, absorbing the water formed in dehydrite, and noting the decrease in pressure. The temperature of the furnace was then raised to 575° and the methane burned. After absorbing the water, the carbon dioxide was measured and then absorbed in ascarite. Any residual nitrogen was noted. This residue serves as a check on any leakages in the system and was found to be negligible in almost all cases. From the corrected pressures before and after combustion, the ratio of carbon dioxide to hydrocarbon was calculated giving n_C, the average number of carbon atoms per molecule of the sample. No attempt was made to determine the hydrogen present in the hydrocarbon.

The fraction volatile at −115° was subjected to a similar combustion analysis. One sample of this material was sealed into a tube and submitted for mass spectrometer analysis.[8]

Methylene Iodide Formation.—Methyl iodide was photochemically exchanged with radio-iodine[9] and the formation of methylene iodide characterized in terms of the activity retained by methylene iodide carrier. It is believed not improper to identify this activity with the formation of methylene iodide, since this is a known product of the photolysis,[10] and since no other fraction probably present should distil with the methylene iodide. Petry[11] has shown that methylene iodide and radio-methyl iodide do not exchange under the conditions of these measurements.

After exchange, the iodine was extracted from the sample, carrier methylene iodide was added in a volume equal to that of the original sample, and the methyl iodide distilled off. Activity due to contaminating radio-methyl iodide was washed out[12] by addition of methyl iodide and subsequent distillation. This operation was repeated until the distillate contained no measurable radioactivity. The methylene iodide was then distilled and a radiochemically pure cut characteristic of this material obtained and counted. The activity appearing in this fraction was compared to that of the original after a correction was made for the difference in the counting efficiency for the two sample densities.

Iodine.—Iodine was determined colorimetrically by observing the optical density at 480, 500 and 520 mμ with the aid of a Beckman DU spectrophotometer.

Results

Gas Analysis.—Data on the combustion analysis of the gas fraction volatile at −196° are given in Table IA. It is seen that very little or no hydrogen is produced in the photolysis and that this fraction represents, very nearly, pure methane.

TABLE IA

ANALYSIS OF METHANE FRACTION

Experiment	3	7	9	13
Sample, moles × 10^6	24.4	52.0	10.6	10.8
Pressure, mm.[a]				
Initial	392	828	170	58
After oxidation at 275°	....	828	....	58
After oxidation at 575°	395	832	170	61
After absorption	3	6	1	2
Combustion, %	99	99	99	98
Hydrogen, %	...[b]	<0.5	...[b]	<1.0
n_C	1.01	1.01	1.00	1.05

[a] All pressures corrected to initial volume. [b] Oxidation at 575° indicates little or no hydrogen.

Combustion analysis of the fraction volatile at −115° gives the results of Table IB. It is seen that this corresponds to a sample which is predominantly C_2.

TABLE IB

ANALYSIS OF ETHANE FRACTION

Experiment	3	7	9	13
Sample, moles × 10^6	8.1	11.8	2.4	2.8
Pressure, mm.[a]				
Initial	130	191	35.6	39
After oxid. at 575°	258	377	69	75
After absorption	2	3	0	2
Combustion, %	98	98	100	95
n_C	1.99	1.99[b,c]	1.94	1.97

[a] All pressures are corrected to initial volume. [b] A duplicate analysis on a second portion of this fraction gives n_C = 2.01. [c] A second ethane fraction of 3.4 μmoles gives n_C = 1.98.

Mass spectrometer analysis of the C_2 fraction (experiment 14, 5.1 × 10^{-6} mole, analysis 913-3) gives the following mole per cent. composition; ethane, 92.4; ethylene, 2.3; acetylene, 0; propane, 0; propylene, 0; C_4, 0; oxygen, 0.3; carbon dioxide, 4.6; methane, 0.2. It is seen that this fraction is predominantly ethane, with perhaps a trace of ethylene. Since ethylene is difficult to determine in the presence of ethane, this may or may not be real. It is believed that the carbon dioxide (em-

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(6) B. M. Norton, THIS JOURNAL, **56**, 2294 (1934).

(7) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

(8) The analytical services of Consolidated Engineering Corp., Pasadena, Cal., were employed.

(9) I^{131} was obtained through the U. S. Atomic Energy Commission, Oak Ridge, Tenn.

(10) W. West and L. Schlessinger, THIS JOURNAL, **60**, 961 (1938).

(11) R. C. Petry, M.S. dissertation, Canisius College, 1953.

(12) R. G. Badger, C. T. Chmiel and R. H. Schuler, THIS JOURNAL, **75**, 2498 (1953).

phasized by the relatively small sample size) was retained by the sample in the initial degassing and released in the degassings at −115° made for this measurement. Characteristically no acetylene, propane, propylene, or higher hydrocarbons are found although the latter three components could easily have been detected and are found in small amounts in analogous radiolytic experiments.[6]

Gas Production.—The total yields of methane, ethane and of iodine for samples initially containing no added iodine are summarized in Fig. 1 as a function of the number of quanta absorbed by the sample. It is seen that the quantum yield for each of these products is constant over the course of the photolysis. The products of the decomposition apparently do not interfere with further decomposition, in spite of the fact that iodine does react, at the concentration levels present here, with the radicals produced in the photolysis.[3]

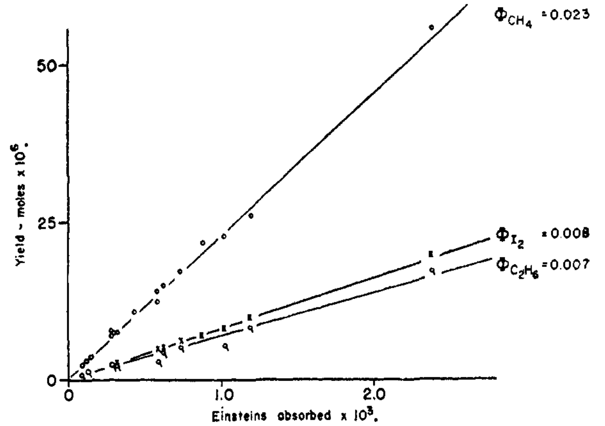

Fig. 1.—Production of methane, ethane and iodine in the photolysis, at 2537 Å., of methyl iodide.

The quantum yield for methane production is constant at 0.023 over the entire region measured with no apparent induction effect or decrease for high irradiation periods. The yields of ethane and of iodine are considerably lower and, on a mole basis, are approximately equal, although that for ethane seems to be consistently about 10% lower than for iodine. This discrepancy may be at least partially due to the difficulty in completely degassing ethane from the sample.[13]

Effect of Temperature.—Methyl iodide was given identical 100 minute irradiations in the thermostated cell at 15, 25 and 40° and the results are given in Table II. These results show that within the reproducibility of the measurements, the temperature coefficient for the production of all products is equal to unity.

TABLE II

EFFECT OF TEMPERATURE

Temp., °C.	Irradiation period, min.[a]	Total yield, moles × 10^6 CH_4	C_2H_6	I_2
13.5	100	7.55	2.9	2.7
25.0	100	6.95	2.6	2.8
40.0	100	7.04	2.5	2.5

[a] 100 min. is equivalent to 283 × 10^{-6} einsteins absorbed.

Effect of Added Iodine.—A number of experiments were performed on samples to which quite high concentrations (up to 10 weight per cent.) of iodine were added before the irradiation, with a decrease in the yields of methane and ethane being observed. The results for the yields relative to those in the absence of iodine are given in Fig. 2 as a function of the mole ratio (I_2/CH_3I). The solid curve represents the functional relationship, $(\phi_0 - \phi)/\phi = 23\ (I_2/CH_3I)$. The data indicate that the effectivity of the iodine in quenching the decomposition is about the same for both methane and ethane production.

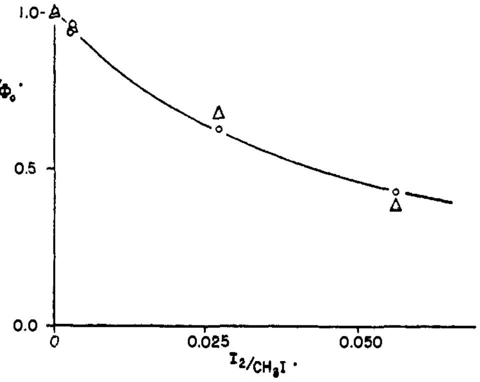

Fig. 2.—Effect of iodine on the gas production yields. Solid curve corresponds to $(\phi_0 - \phi)/\phi = 23\ I_2/CH_3I$. Circles refer to methane production; triangles to ethane production.

Experimentally these results are somewhat difficult to obtain, as it is observed that the transmission of the cell window decreases during the course of the irradiation of solutions containing iodine. This decrease in transmission, due to a product being deposited on the cell window, has not been observed for solutions in which iodine has not been initially dissolved. The relative yields have been corrected to correspond to the average energy absorbed during the irradiation. It was found possible to restore the irradiation cell to its original transparency by pumping while heating the quartz to red heat. Once the aforementioned deposit forms, it appears to behave autocatalytically, absorbing light itself and producing further discoloration.

The quenching of the gas production reactions is believed to be due to absorption of the energy by iodine rather than by the methyl iodide. The molar extinction coefficients of iodine and methyl iodide in *n*-heptane have been determined at 2537 Å. to be 450 and 400, respectively, and cannot account for the observed effectivity of the iodine. Iodine is, however, highly solvated in methyl iodide with a very intense absorption of the solvated complex being observed in the region around 300 mμ.[14]

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[13] It will be noted that G. Emschwiller, *Compt. rend.*, **192**, 799 (1931), claims that only methane is produced in the photolysis. Earlier A. Job and G. Emschwiller, *ibid.*, **179**, 168 (1924), found that hydrogen, methane, ethane and ethylene were formed. Since in the absence of other reactants capable of removing the radicals such as oxygen, net iodine production can only result from processes producing carbon-carbon bonds, it is expected that molecular iodine and ethane should be formed in equal yields. Our experiments show no hydrogen and little ethylene. *Cf.* also R. Spence and W. Wild, *Proc. Leeds. Phil. Soc.*, **3**, 141 (1936).

[14] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952), estimate an extinction coefficient of 30,000 at 295 mμ for the solvated complex.

It is not impossible that the extinction coefficient of the complex be greater than 10,000 at 254 mμ, a value which would be in agreement with the required inner filter effect. Confirmation awaits the measurement of the absorption of the iodine–methyl iodide complex at 2537 Å.

Methylene Iodide Formation.—The results of the radio-methylene iodide carrier experiments are given in Table III. These results are considerably lower than given previously (~4–5%) and are believed to be much more accurate due to the greater care possible through the use of iodine-131. If it is assumed that the quantum yield for total exchange is approximately unity,[3] then the fraction of the activity appearing as methylene iodide corresponds to the quantum yield for the formation of this product *via* the reactions

$$CH_3\cdot + CH_3I \longrightarrow CH_4 + CH_2I\cdot \qquad (4)$$

$$CH_2I\cdot + I_2^* \longrightarrow CH_2I_2^* + I\cdot \qquad (8\text{-R})$$

TABLE III

FORMATION OF METHYLENE IODIDE

Carrier[a] iodine, moles $\times 10^6$	Irrad. period, min.[c]	Exch., %	Activity[b] Org.	CH_3I	CH_2I_2	Resid.[d]	Yield, CH_2I_2/org.
36	100	97.5	4140	3975	63	58	0.015
66	50	81.5[e]	4643	4382	62	61[f]	.013

[a] In 5 ml. of sample. [b] Counts per min. corrected for dilution and self absorption (activity in CH_3I/activity in CH_2I_2 = 1.26). [c] At 7.8 × 10^{-6} einsteins/min. [d] Stillpot residue (2–3 ml.) diluted and counted; shows no concentration of activity over that in CH_2I_2. [e] Corresponds to a quantum yield of 0.6 (in the absence of stirring). [f] Stillpot rinsed with 5 ml. of acetone; negligible activity in this fraction.

The yield of 0.013 is somewhat lower than anticipated from the higher methane quantum yield (0.023), since, if reaction 2 ensues upon reaction 1, the two should be stoichiometrically equal.

Discussion

The present investigation has carried the measurement of the photodecomposition of methyl iodide into a region of iodine concentration far beyond the point at which iodine is known to react almost quantitatively with the radicals produced in the photolysis.[3] The results show that the presence of iodine is not effective in quenching the reactions which result in the observed decomposition. Measurements of the effect of temperature on the processes involved show that the reactions producing methane, ethane and iodine are not temperature dependent in the region around 25°.

Any mechanism proposed as an explanation of the photodecomposition of methyl iodide must be consistent with the above facts and with the fact that the reactions are wave length dependent, in general increasing with decreasing wave length. Also, the existence of decomposition reactions which are independent of iodine concentration, in spite of important iodine quenching reactions, must be resolved in terms of a mechanism which permits the formation of products along two different reaction paths. The relative importance of these different paths must then be given in terms of a "splitting ratio" which is determined by the probabilities of the different reactions.

It is believed that the hot radical reactions postulated for the photolysis of methyl iodide[3,4] are not inconsistent with any of the known facts and offer a plausible explanation for the observed reactions. Such reactions differ from ordinary thermal reactions only in that the energy distribution of the reacting species is such that there is a relatively large population of the extra-thermal portion of the energy spectrum. The hot radical mechanism proposed for the photodecomposition of methyl iodide attributes the reactions to processes which involve these extra-thermal methyl radicals before they had an opportunity to lose this excess kinetic energy. That such radicals (with an energy of the order of 35 kcal./mole) are produced is seen in a consideration of the energy involved in the excitation process occurring at 2537 Å. At this wave length, the excitation takes place to a dissociative upper state and results in the production of a methyl radical and an excited iodine atom.[15] The difference between the quantum energy and the energy required to dissociate the C–I bond and excite the iodine atom appears as translational energy, most of which is retained by the radical as required by conservation of momentum. While this energy is certainly sufficient to give rise to the observed reactions, the question is whether or not the probability of the proposed reactions is sufficiently high to permit competition with the moderation process. In this respect the process involved may be regarded as analogous to side reactions encountered during the thermalization of high energy neutrons. Theoretical calculations based on this analog suggest themselves as being capable of providing further information concerning the present problem if the required cross sections can be properly estimated. Since, in hot radical reactions, the distribution of energies in reacting species is non-Boltzmannian, and independent of temperature, it is expected (and found in the photolysis of methyl iodide) that the reactions should have a temperature coefficient not different from unity.

The following mechanism is proposed as being consistent with all of the presently known facts

$$CH_3I \xrightarrow{h\nu} CH_3\cdot + I\cdot \qquad (1)$$

$$CH_3\cdot + M \longrightarrow CH_3\cdot + M' \qquad (2\text{-H})$$

$$CH_3\cdot + I_2 \longrightarrow CH_3I + I\cdot \qquad (3)$$

$$CH_3\cdot + CH_3I \longrightarrow CH_4 + CH_2I\cdot \qquad (4\text{-H})$$

$$\longrightarrow CH_3I + CH_3\cdot \qquad (5\text{-H})$$

$$\longrightarrow C_2H_6 + I\cdot \qquad (6\text{-H})$$

$$CH_2I\cdot + CH_3I \longrightarrow CH_2I_2 + CH_3\cdot \qquad (7)$$

$$CH_2I\cdot + I_2 \longrightarrow CH_2I_2 + I\cdot \qquad (8)$$

$$I\cdot + I\cdot \longrightarrow I_2 \qquad (9)$$

In this mechanism, the splitting ratios controlling the decomposition are the ratios of the relative probabilities of reaction 2 and reactions 4, 5 and 6. Reaction 5, originally omitted from the mechanism, is included here in order to complete the possibilities of the hot radical reactions and to provide a basis for work in solutions. The net effect of this reaction is moderation, although the cross section may be considerably different than that of thermal moderation. Reaction 7 is included in order to account for the discrepancy between the formation of

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[15] G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

radio-methylene iodide and methane. There is some possibility that the $CH_2I\cdot$ radical decomposes before reacting with iodine. However if this occurs, this should result in a higher radiomethylene iodide yield or a quantum yield of ethylene greater than the observed value of less than 0.0002.

It will be observed that the above mechanism eliminates, except for the recombination of iodine atoms, all reactions which are second order in radicals. This is necessary since the radicals are quickly removed by reaction with the iodine and are therefore present only at very low concentration levels. This is one point of departure between our proposal for the liquid phase photolysis and that of Schultz and Taylor in studies of the vapor phase. We postulate that ethane results from a hot process (reaction 6-H) while Schultz and Taylor prefer to regard it as being formed by the combination of methyl radicals. This latter process can be of greater importance in the vapor phase because of a relatively low concentration of iodine. Recent work on the flash photolysis of methyl iodide by Davidson and Carrington[16] further indicates the importance of methyl radical combination in the vapor phase at very high light intensities.

Acknowledgment.—The authors wish to thank Professor William H. Hamill of the University of Notre Dame for numerous discussions on the subject. One of us (C. T. C.) is indebted to the Research Corporation for the grant of a fellowship.

[16] N. Davidson and T. Carrington, THIS JOURNAL, **74**, 6277 (1952).

BUFFALO, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

The Radiolysis of Liquid Methyl Iodide[1]

BY ROBERT C. PETRY AND ROBERT H. SCHULER[2]

RECEIVED FEBRUARY 20, 1953

Hydrogen, methane, ethane, ethylene and acetylene have been observed as gaseous products in the 100 kev. X-ray decomposition of liquid methyl iodide. The respective yields are found to be, relative to the yield of iodine as unity, equal to 0.067, 0.47, 0.90, 0.067 and 0.026 and are directly proportional to the total irradiation dose given the sample. The formation of trace amounts of higher hydrocarbons is indicated in the mass spectrometer analysis of the less volatile fractions. Methylene iodide and ethyl iodide are shown to be minor products of the radiolysis. In the presence of large amounts of iodine (1–20 mole per cent.) the yield of gaseous products decreases, with the effectivity of the iodine in quenching the reactions varying for the different products. The relative yields observed for decomposition produced by very low intensity Co^{60} γ-radiation are found to be identical to those given above for the more intense X-radiation. The absolute decomposition yields are in approximate agreement with the values obtained in fast-electron bombardment. The relatively high yield of ethane and iodine, together with other complications evidenced by the formation of ethylene, acetylene and higher hydrocarbons, indicates very strongly the importance of ionic processes in the over-all decomposition.

Lefort, Bonet-Maury and Frilley[3] have studied iodine production in the decomposition of air saturated liquid ethyl iodide by X-radiation and by radon alpha particles. Sue and Saeland[4] have studied the same process in various alkyl iodides using the mixed fast neutron–gamma radiation from a 300 mc. radium–beryllium source, and Schuler and Hamill[5] have observed the fast-electron and X-radiation induced processes using a 1-2 mev. Van de Graaf generator as the source of radiation. It was evidenced in this previous work[5] that the yield of iodine in the radiolysis of methyl iodide is much greater than anticipated from the low quantum yield for iodine production observed in the photodecomposition. The purpose of this investigation was to obtain information on the gaseous products of the radiolysis and to compare the yields to these observed in the photolysis of the same system.[6]

Experimental

Methyl Iodide.—The methyl iodide samples were from the same preparations used in the photolytic work.[6] The boiling point was 42.4° and the refractive index ($n^{25}\mathrm{D}$) 1.5271–1.5272.

Irradiation.—The unfiltered radiation from a line operated, industrial X-ray unit with a tungsten target was used as the major source of activation. The instrument was operated at a constant intensity characterized by a current of 5 ma. at 120 pkv., the effective wave length of the radiation being in the region of 0.2–0.4 Å. The current was maintained at a constant value electronically and was monitored on a recording milliammeter. Variations in line voltage could be compensated for by a manual adjustment of the transformer setting.

The samples (10 ml.) were contained in a 50-ml. florence flask to which a high-vacuum stopcock and ground joint had been affixed for ease of attachment to the vacuum line. These were irradiated in the position of maximum X-ray dosage by placing the cell in the well of the tube with the radiation entering vertically through the bottom of the cell. During irradiation the sample temperature rose slightly due to heat transferred from the X-ray tube. A blower circulated air over the cell to keep this temperature rise to a minimum. No other temperature control was attempted. Utilizing this arrangement the reproducibility in positioning the sample was very good. The limiting factor in these investigations is the constancy in the intensity out-put of the X-ray tube. Our measurements indicate that this is controlled to within ±2%.

In the case of expt. 31, the radiation from 300 millicuries of Co^{60} was used for activation. The irradiation vessel consisted of a cylindrical tube with an attached break-off seal through which the sample could be attached to the vacuum line after irradiation, and a square Pyrex absorption cell which was used for measurement of the iodine concentration during the course of irradiation.

In reporting the results, the reaction yields are given in terms of moles of reaction product per unit of irradiation at the constant intensities described above. Both experimen-

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[1] From the M.S. Dissertation of R. C. Petry, Canisius College, June 1953. This work was supported, in part, under Contract AT(30-1)-1084 with the U. S. Atomic Energy Commission.

[2] Brookhaven National Laboratory, Upton, N. Y.

[3] M. Lefort, P. Bonet-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948).

[4] P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949).

[5] R. H. Schuler and W. H. Hamill, THIS JOURNAL, **74**, 6171 (1952).

[6] R. H. Schuler and C. T. Chmiel, *ibid.*, **75**, 3792 (1953).